

TWO STAGE PROCESSING OF POST CONSUMER PLASTICS WITH COAL

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ABSTRACT

Coprocessing of coal with plastics oil from Conrad Industries and post-consumer plastics from Germany was performed to evaluate the effect of first stage waste plastics processing on the final products obtained from the two stage processing of waste plastics with coal. The plastics oil was obtained from the pyrolysis of waste plastics, and yielded an oil with a considerable amount of light materials that were removed by distillation prior to use. The heavier fraction from the plastics oil was coprocessed with the coal. The post consumer plastics which were introduced as solids were processed at 440 °C for 60 min, with 2.75 MPa of H_2 , introduced at ambient temperature, and a first stage catalyst which was either HZSM-5 or Low Alumina. For both sources of plastics, the second stage reaction, in which the liquid plastics from the first stage were combined with coal, was performed at 400 °C using either Fe or Mo naphthenate slurry phase catalyst precursors. The effect of the waste plastics sources and processing on the product distribution and the boiling point distribution from coprocessing with coal was evaluated and compared.

INTRODUCTION

Post consumer plastics are waste materials that are usually disposed of in land-fills. The feasibility of taking waste plastics from actual waste streams and converting them to usable materials, such as fuels and chemical feedstocks, is important for minimizing waste and fully utilizing our natural resources. These post-consumer plastics contain not only the polymers composing the plastics, but also the compounds that have been added to serve as antioxidants and fillers. Hence, these plastics, both because of the composition of the plastic itself and because of the variety in the mixture composition, may have different liquefaction properties and characteristics to those of the pure polymer. The available supply of post-consumer plastics is relatively small and, if converted to a liquid fuel, would only produce an annual amount that was sufficient to provide a one month's supply of fuel for the United States. (Techline, 1996)

Previous research has been performed investigating the coprocessing of waste plastics with coal. The results showed that single stage reactions of these disparate materials were difficult, as neither the reaction conditions nor the catalysts could be tailored simultaneously for both materials. (Luo and Curtis, 1996a,b) Subsequent research involved the two stage processing of coal and waste plastics such that the waste plastics were reacted in the first stage at conditions that promoted their conversion to liquids. (Ding et al, 1996; Luo and Curtis, 1996c) The liquid products obtained were then used as a solvent and reacted with coal in a less severe second stage reaction that used hydrotreatment catalysts designed to promote the liquefaction of coal. The second stage reaction temperature affected the breakdown of the waste plastics solvent and, if too high, would result in substantial gas production. (Luo, 1997)

This study investigated the effect of the type of first stage processing and the source of waste plastics on waste plastics coprocessing with coal. Two different types of first stage processing were investigated. The first type of processing consisted of pyrolyzing waste plastics in the Conrad Industries' process. (Meszaros, 1994) The pyrolyzed oil produced was the source of the plastics oil used in this research. The second type of first stage processing was the liquefaction of post consumer plastics, which came from households and businesses in Germany. The oil from both of these processes was used as the solvent for the coal in the second stage coprocessing reactions.

EXPERIMENTAL

Two batches of post consumer waste were obtained. The first, from Conrad Industries, was a pyrolysis liquid produced from post-consumer plastics. The second was obtained from Germany, and was composed of post-consumer plastics that had been collected and extruded to increase their

density. The European plastics mixture was supplied by Dr. Gerald P. Huffman of the University of Kentucky, and contained small amounts of other materials such as Al granules, Al foil and paper which were removed prior to reaction. Illinois No. 6 coal, obtained from the Argonne Premium Coal Sample Bank, was used as received.

In this study, slurry phase hydrotreating catalyst precursors, Mo naphthenate (MoNaph) and Fe naphthenate (FeNaph), were used for the reaction of distilled Conrad plastics oil and coal, and for the second stage reaction of the European plastics with coal. A fluid cracking catalyst, Low Alumina, and a zeolite, HZSM-5, were used individually in the first stage processing of the waste plastics. Both HZSM-5 and Low Alumina catalysts were pretreated prior to being used in the reaction by heating for 2 hr at 477 K followed by 2 hr at 811 K.

Reactions. Before the Conrad plastics oil was used as a coprocessing solvent for coal, it was distilled at 90 °C under 30 mm of Hg to remove the light fractions. The residual fraction was used as a coprocessing solvent. The coprocessing reaction was performed with 2 g of coal and 2 g of distilled Conrad oil in 20 cm³ stainless steel microtubular reactors at 713 K for 30 min. The reactors were charged with 5.6 MPa of H₂, introduced at ambient temperature, and were agitated horizontally at 435 rpm during the reactions. Slurry phase catalyst precursors, MoNaph and FeNaph, were introduced at 1000 ppm of active metal with 6000 ppm of elemental sulfur on a total reactant basis.

The European plastics mixture was reacted in the first stage in 50 cm³ stainless steel microtubular reactors at 713 K for 60 min under an initial H₂ pressure of 2.8 MPa, introduced at ambient temperature. The reactors were agitated vertically at 450 rpm. Ten grams of plastics mixture were charged to the reactor with 10% Low Alumina or HZSM-5 on a total plastics charge basis. The hexane soluble fraction produced from the first stage was used as the solvent for the second stage. The second stage reaction was performed using the same procedures and conditions as those used for the distilled Conrad oil and coal.

Product Analysis. The liquid products from the coprocessing reactions were analyzed by solvent fractionation using hexane as the initial solvent followed by tetrahydrofuran (THF). The amount of gas, hexane, and THF soluble and insoluble materials produced, was determined. The total boiling point distribution of the reaction products after coprocessing was also determined by combining analyses of the product distribution with that of simulated distillation of the hexane soluble fraction.

RESULTS AND DISCUSSION

Conrad Waste Plastics Oil. The research performed evaluated the effect of the type of first stage processing and of the source of waste plastics used in the first stage. The first set of experiments that were performed involved using the pyrolysis product from the Conrad Industries waste plastics pyrolysis process as the coprocessing solvent. The plastics oil produced contained a substantial amount of light materials that were distilled prior to the coprocessing reactions. Hence, in these experiments the Conrad process was effectively the first stage process. The distilled Conrad oil was then used as the second stage coprocessing solvent.

Three types of reactions were performed: thermal, catalytic with FeNaph and excess sulfur, and catalytic with MoNaph and excess sulfur. The presence of a catalyst had a pronounced effect on the amount of each fraction, hexane solubles, THF solubles and insoluble organic material (IOM) produced. Thermal coprocessing reactions yielded the lowest conversions and catalytic coprocessing reactions with MoNaph yielded the highest conversions. The two catalysts had different effects on the reaction product obtained. The slurry phase FeNaph and excess sulfur produced a larger amount of hexane solubles, while MoNaph produced a larger amount of THF solubles. The coprocessing reaction with MoNaph converted 90.4% of the solid coal to THF solubles, while the high total recovery of 91.5% indicated that few volatiles were produced. By contrast, the coprocessing reactions with FeNaph did not convert as much coal, yielding an 82.8% conversion, and also had a somewhat lower total recovery of 86.8%, which indicated that FeNaph had a greater propensity for producing volatiles from the plastics oil solvent than did MoNaph.

The total boiling point distributions from these reactions compared well with the results from the product distributions (Table 2). The amount of volatiles that are shown in the <100 °C fraction

are the highest for the reactions with FeNaph and the lowest for the thermal reactions. The amount of material boiling between 100 and 500 °C was greatest for the coprocessing reactions containing MoNaph and excess sulfur. When the results are viewed in terms of the overall heaviness of the reaction product, the thermal reactions contained the most material 87.0% in the >500 °C range and the IOM while the reactions with FeNaph and MoNaph produced similar amounts of 69.7 and 70.4%, respectively. The reaction with FeNaph resulted in less material being converted to THF soluble material than did the reactions with MoNaph.

European Waste Plastics. The second material used in this study was post-consumer waste plastics that had been collected and concentrated for transportation to processing plants. The first stage reaction was performed using hydrocracking catalysts, either HZSM-5 or Low Alumina, to shorten the polymeric chains and produce a liquefied product. The reaction was performed at a temperature of 440 °C with a low H₂ pressure, to promote hydrocracking. These conditions were chosen because the less severe conditions did not convert the solid European waste plastics into hexane soluble materials, and because more severe conditions would result in a substantial portion of the waste plastics being converted into gases or highly volatile liquids. After the European waste plastics were reacted in the first stage, the hexane soluble fraction was used as the solvent for the second stage processing with coal. The second stage reaction was performed with a slurry phase hydrotreating catalyst, either FeNaph or MoNaph and excess sulfur.

The product distributions from the second stage coprocessing reaction of the hexane soluble fraction of the European waste plastics reacted with coal showed little effect due to either the first stage or the hydrotreating catalyst (Table 3). The conversions from the second stage reactions using HZSM-5/FeNaph and Low Alumina/FeNaph yielded very similar conversions of 83.3 and 84.7%, respectively. The conversions from the second stage reactions with MoNaph were slightly higher, 87.1% for HZSM-5/MoNaph and 88.0% for Low Alumina/MoNaph. Some differences were observed in the product distribution. The hexane solubles for the second stage reactions with FeNaph averaged 19.5% and were lower than the average of 25.0% produced from the reactions with MoNaph. The second stage reactions with FeNaph were not as effective as those with MoNaph for converting the reactants to hexane soluble or THF soluble material.

The boiling point distributions from the two stage processing of European waste plastics and coal were calculated by combining the simulated distillation results from hexane solubles produced in the second stage with the product distributions from the combined first and second stages. The total boiling point distributions, given in Table 4, show a bimodal distribution of the reaction products. The products were either gases or light hydrocarbons boiling at <100 °C, or extremely heavy material with boiling points of >500 °C, or IOM. The HZSM-5 first stage products, when introduced as a solvent for the second stage coal reaction, resulted in less IOM from the two stages than in the two stage reactions using Low Alumina as the first stage catalyst.

SUMMARY

Two stage coprocessing of waste plastics with coal was found to be affected by the source of waste plastics and by the type of first stage processing. Pyrolysis as the first stage process cracked the polymeric molecules into much smaller molecules, forming gases, liquids and some residual solids. The oil fraction contained a considerable amount of light materials which were removed by distillation prior to its use as a second stage solvent for coal. Similarly, the removal of the heavy plastics material from the Conrad plastics oil by the pyrolysis process yielded a solvent that was inherently lighter and, hence, resulted in less heavy products in the second stage process than the liquefaction solvent. By contrast, the first stage liquefaction of the European plastics was a less severe first stage condition. Even though only the hexane fraction of the first stage products was used as the solvent in the second stage coprocessing reaction, that solvent contained a heavier product slate than did the Conrad plastics oil. Overall conversion from two stage coprocessing reactions with corresponding catalysts was reduced when a liquefaction first stage was used rather than a pyrolysis first stage.

The more active Mo naphthenate catalyst promoted higher second stage conversions than Fe naphthenate regardless of the first stage material. The second stage conversions from reactions in which Conrad plastics oil and liquefaction were used as the first stage process were quite similar when Mo naphthenate was used as the second stage catalyst. Fe naphthenate showed a lower activity than Mo naphthenate for promoting conversion, regardless of first stage processing. When

liquefaction was used as the first stage, the overall conversion from two stage processing was reduced due to the substantial amount of waste plastics that remained unconverted in the first stage. It is highly likely that this material would be converted if it were recycled (Joo and Curtis, 1997). The catalyst present in the first stage also affected the overall conversion from two stage processing. HZSM-5 was a more effective catalyst for promoting first stage and overall conversion than was Low Alumina.

References

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Table 1. Product Distributions from Coprocessing Reactions of Distilled Conrad Plastics Oil and Illinois No. 6 Coal

| Reaction System | Product Distribution, (wt %) | | | | Conversion (%) | Recovery (%) |
|-----------------|------------------------------|-----------------|--------------|------------|----------------|--------------|
| | Gas | Hexane Solubles | THF Solubles | IOM | | |
| Thermal | 5.5 ± 0.2 | 7.8 ± 1.0 | 60.1 ± 0.2 | 26.2 ± 1.0 | 73.8 ± 1.0 | 95.0 ± 1.1 |
| FeNaph | 5.8 ± 0.2 | 32.3 ± 1.9 | 44.7 ± 1.5 | 17.2 ± 0.6 | 82.8 ± 0.6 | 86.8 ± 1.6 |
| MoNaph | 5.3 ± 0.8 | 30.3 ± 2.6 | 54.8 ± 3.8 | 9.6 ± 0.4 | 90.4 ± 0.4 | 91.5 ± 2.2 |

Table 2. Boiling Point Distributions from Coprocessing Reactions of Distilled Conrad Oil and Illinois No. 6 Coal

| Reaction System | Boiling Point Distribution (%) | | | | |
|-----------------|--------------------------------|---------|------------|---------|------|
| | Gas | <100 °C | 100-500 °C | >500 °C | IOM |
| Thermal | 5.8 | 5.0 | 3.1 | 60.8 | 26.2 |
| FeNaph | 5.8 | 13.3 | 11.2 | 52.5 | 17.2 |
| MoNaph | 5.3 | 8.6 | 15.7 | 60.8 | 9.6 |

**Table 3. Product Distributions from Coprocessing Reactions of
European Waste Plastics with Illinois No. 6 Coal**

| First Stage Catalyst | Second Stage Catalyst | Production Distribution (wt%) | | | | Conversion (%) | Recovery (%) |
|----------------------|-----------------------|-------------------------------|-----------------|--------------|------------|----------------|--------------|
| | | Gas | Hexane Solubles | THF Solubles | IOM | | |
| HZSM-5 | FeNaph | 4.1 ± 0.0 | 18.9 ± 1.4 | 60.3 ± 2.0 | 16.7 ± 0.6 | 83.3 ± 0.7 | 83.1 |
| L Alumina | FeNaph | 4.1 ± 0.1 | 19.5 ± 0.7 | 61.1 ± 1.7 | 15.3 ± 1.0 | 84.7 ± 1.0 | 88.3 |
| HZSM-5 | MoNaph | 4.1 ± 0.1 | 24.7 ± 0.4 | 58.3 ± 0.4 | 12.9 ± 0.7 | 87.1 ± 0.7 | 90.3 |
| L Alumina | MoNaph | 3.7 ± 0.1 | 25.2 ± 0.2 | 59.1 ± 1.3 | 12.0 ± 1.6 | 88.0 ± 1.6 | 87.7 |

**Table 4. Boiling Point Distribution from Coprocessing Reactions of
European Waste Plastics with Illinois No.6 Coal**

| Reaction System | Boiling Point Distribution (wt%) | | | | |
|-----------------|----------------------------------|---------|------------|---------|------|
| | Gas | <100 °C | 100-500 °C | >500 °C | IOM |
| HZSM-5/Fe | 9.1 | 15.1 | 0.0 | 52.4 | 23.6 |
| Alumina/Fe | 7.9 | 9.4 | 0.0 | 54.1 | 28.7 |
| HZSM-5/Mo | 9.1 | 16.6 | 0.0 | 53.0 | 21.2 |
| Alumina/Mo | 7.6 | 12.0 | 0.0 | 53.6 | 26.7 |